HAMILTON HARBOUR

TRACE CONTAMINANTS - 1982-83

LOADINGS TO, AND CONCENTRATIONS IN THE HARBOUR

June, 1986

Ontario
Ministry of the Environment

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SECOND EDITION

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1.0 SUMMARY AND CONCLUSIONS

1. Water and suspended sediment samples were collected from the Hamilton and Burlington STP's and from six locations in Hamilton Harbour during the summer of 1982. These were analyzed for heavy metals, PCB's and organochlorine pesticides. Bottom sediment samples were collected on one occasion and analyzed for PCB's, pesticides and PAH's.

2. The most frequently found trace organic contaminants in the STP effluents and the harbour water were the BHC isomers, HCB and PCB's. Percentages of samples with positive detection in the Hamilton STP, Burlington STP and harbour water respectively were: PCB's, 50, 27 and 14%; α-BHC, 71, 67 and 92%; β-BHC, 43, 33 and 14%; γ-BHC, 64, 80 and 69%; and HCB, 57, 60 and 25%. Harbour PCB's and γ-BHC exceeded Provincial Water Quality Objectives 14% of the time.

3. Except in the northeast corner and Burlington Ship Canal, the harbour sediments exceed the Ministry guideline for open water disposal of PCB's, with average concentrations of 440 ng/g and maximum concentrations of 1270 ng/g. Spatial variation of sediment PCB's was irregular and not coordinated with previous years. Chlordane and the BHC's were frequently found in minor amounts.

4. The harbour sediments are highly contaminated with PAH's. Spatial distribution suggests that the steel companies are the major source of PAH's, and the Hamilton STP is a minor source.

5. The distribution of PCB's in the harbour water is consistent with the Hamilton STP being a major source. However, BHC's are uniformly distributed in the harbour, and lake data suggest there is no obvious local source of these compounds.

6. Heavy metal loadings from the STP's vary over a wide range with time, both on a short-term (hourly) and long-term (weekly) basis. Average data suggest a decrease in loadings for copper, zinc and chromium since 1977 at the Hamilton STP, and unchanged loadings for the other metals. At the Burlington STP, iron loading is increased due to the use of ferric chloride for phosphorus removal.

7. The loadings of different metals from the Hamilton STP were more highly correlated with each other than those from the Burlington STP, both on an hourly and a weekly basis. This is as expected considering the major industrial input of metals in Hamilton compared to the primarily residential sources in Burlington. However, effluent concentrations for several metals are not significantly different between the two plants.

8. In the harbour water, copper exceeded Provincial Water Quality Objectives two-thirds of the time. Iron, zinc and cadmium exceeded Objectives on a less frequent basis. All heavy metals exhibited highest concentrations in the southeast part of the harbour.

9. Limited comparisons with 1980 data indicate significant reductions in concentrations of Cu, Fe, Zn and Mn. Other metals showed no significant change.

10. Only manganese showed any consistent variation with depth and season, with hypolimnetic concentrations increasing as hypolimnetic anoxia spreads. Following autumn overturn, manganese concentrations dropped to lower values.

11. The fraction of heavy metals in the particulate phase in harbour samples was highly irregular. Only for zinc, iron and manganese was a significant fraction of particulate material indicated by comparing concentrations of centrifuged water samples with those of total samples.

12. Samples of suspended sediment were partitioned into five fractions representing different chemical forms and hence different levels of bioavailability. The residual (unavailable) phase dominated the speciation of Co and Fe, and co-dominated with the organic phase for Cr, Cu and Ni. The reducible (Fe-Mn oxide) phase was important for Zn, Pb and Mn, but other phases were also important for these metals. Manganese was apparently the most highly available metal with a large fraction in the surface oxide-carbonate phase.

2.0 RECOMMENDATIONS

1. Guidelines for non-conventional pollutants in STP effluents should be established, based on concentrations achieved in representative well-operated conventional activated sludge treatment plants in Ontario (i.e. establishing Best Available and Practicable Technology).

2. Improved methods for removing contaminants from STP influents, with emphasis on organic parameters, should be assessed for large-scale application.

3. Sediment criteria for dredge spoil disposal for trace organic parameters other than PCB's should be established and disposal requirements set to eliminate dredge wastes in the most effective manner.

3.0 BACKGROUND

Within recent years, the public has become increasingly aware of the hazards posed by toxic contaminants in the Great Lakes. Such persistent toxic substances can include both heavy metals and a large range of organic substances, many of which are broken down at exceedingly slow rates and may, therefore, persist for years in the environment.

The major emphasis of the Ministry studies in Hamilton Harbour to date has been directed towards eutrophication and the oxygen depletion problem (MOE 1985). Only for heavy metals in sediments was any great body of data established during the intensive years of study (1975-80). These studies showed the harbour sediments to be above the Ministry dredge disposal guidelines for almost all heavy metals; concentrations were highest in the deep central areas of the harbour and in shallow zones adjacent to major outfalls (MOE 1985).

Sediment samples were collected by dredge in 1975, 1977 and 1978, and analyzed for PCB's and organochlorine pesticides. PCB's were found in nearly all the samples collected, though at widely varying concentrations. PCB concentrations at stations 258 and 4 were consistently higher than those at stations 252 and 270 (Fig. 1). High concentrations (500-1800 ng/g) were also observed at stations 267, 256, 20 and 268 in the southeast corner of the harbour. By contrast, most samples from the north shore or west end of the harbour contained 30 to 200 ng/g PCB's. DDT and/or its metabolites were found in about half of all samples, and chlordanes were detected in approximately one-quarter of the samples. Most of these positive detections were also in the southeast corner or central deep area of the harbour. Other pesticides were found only occasionally or not at all.

In the water column, detailed results were available only for iron and zinc. Average zinc levels exceeded the Ministry's Provincial Water Quality Objectives, while iron levels were close to, and

occasionally exceeded the Objectives. Few measurements existed for other metals, and many of these were below detection limits. Improved analytical techniques in 1980 lowered the detection limit for trace metals, and preliminary measurements suggested that the average concentrations of Cu, Cd and Hg, and maximum concentration of Pb exceeded Ministry guidelines.

A limited series of water samples was collected in 1975 and analyzed for PCB's and pesticides. Thiodan I (endosulfan I) was found in approximately one-third of the samples, with an average concentration of 0.007 ug/L and a maximum concentration of 0.030 ug/L. Other contaminants were found only once in the series of 24 samples, or not at all. These findings were inconsistent with the larger extent of contamination observed in the sediments; at any rate, they were based upon too few samples to draw a firm conclusion. Hence, a need existed for further information on trace organic contaminant concentrations in the harbour water and sediments.

The loadings of heavy metals to the harbour from all sources in 1977 have been summarized (MOE 1985). These results showed that the steel industries (Stelco and Dofasco) were the principal source of copper, zinc, manganese, chromium and iron, although small amounts of these metals were also contributed by the STP's (mainly Hamilton STP), Cootes Paradise and the various runoffs. Cadmium was contributed by the Hamilton STP, Cootes Paradise and the runoffs, while similar amounts of lead originated from all major sources. As the steel companies discharge process wastes through the Hamilton sewage system, contributions of these metals from the Hamilton STP largely originated from the industries. Phenol and cyanide were also included in the 1977 study and its 1979 update, (MOE 1985) and originated almost exclusively from the steel companies.

Only very limited information is available on trace organic contaminant loadings to Hamilton Harbour. Several water samples taken in 1981 from the Strathearne St. slip, a former location of a transformer manufacturing site, showed PCB's to be consistently

present, at concentrations of 0.46 to 5.3 ug/L and as high as 180 ug/L of PCB. PCB's were seldom detected, however, in Red Hill Creek, with a maximum concentration of 0.05 ug/L observed during runoff.

Two 1979 samples of Hamilton STP effluent and one sample of Burlington STP effluent were analyzed by GC/MS for a range of organic contaminants. Among the substances found were aromatic hydrocarbons, chlorinated and brominated aliphatic and aromatic hydrocarbons, di-octyl phthalate, caffeine, alkylated phenols, and miscellaneous ketones and steroids. Another sample of the Burlington STP effluent analyzed in 1981, however, showed no pesticides and only traces (0.5 ug/L) of a few of the above compounds.

Approximately 40 polynuclear aromatic hydrocarbons (PAH's) were identified in a limited range of samples from the Hamilton STP, Stelco and Dofasco in 1978. Concentrations in the STP effluent ranged from 0.02 to 0.3 ug/L; similar concentrations occurred in the diluted coke plant discharges to the harbour.

While indicating the existence of problems, these limited programs provided insufficient information to quantify the inputs to, concentrations in, and retention of trace contaminants in Hamilton Harbour. Accordingly, a sampling program was undertaken in 1982 and 1983 to measure the concentrations of heavy metals, PCB's, organochlorine pesticides and PAH's in the STP effluents and the harbour water and suspended material. Information obtained in a study of the Hamilton STP by the Water and Wastewater Management Section was coordinated with the present study to provide an improved picture of trace contaminant loadings from the Hamilton STP.

4.0 SCOPE

The projects discussed in the report fall into two categories: (a) trace contaminant loadings to Hamilton Harbour, and (b) trace contaminants in Hamilton Harbour water and sediments. Each of these will be discussed in turn.

4.1 Trace Contaminant Loading to Hamilton Harbour

Studies concentrated on the two municipal sewage treatment plants that discharge directly to the harbour: the Hamilton and Burlington STP's. Weekly 24-hour composite samples of the final effluents were collected from each STP from late May to September 1, 1982. Similar composite samples were collected from the Burlington STP from January to April, 1983. Samples were analyzed for Fe, Mn, Cd, Cr, Cu, Ni, Pb, Zn, PCB's, organochlorine pesticides and suspended solids. Biweekly samples from each STP during the summer were centrifuged and the solid residues partitioned into five fractions according to a sequential chemical extraction procedure (Tessier 1979). These fractions were exchangeable metal ions, surface oxide and carbonate-bound ions, ions bound to Fe-Mn oxides, ions bound to organic matter and sulphides and residual metal ions. The extractions were performed by K. R. Lum of the Canada Centre for Inland Waters. During two 12-hour periods in summer 1982, grab samples were collected from each STP every half hour by automatic samplers, and analyzed for the above-mentioned heavy metals. One period represented dry weather and the other, a runoff event. On one occasion, the final effluent from the Hamilton STP was passed through a polycarbonate membrane filter, and the solid material examined semiquantitatively for heavy metals by SEM/EDXRA (scanning electron microscope/energy dispersive x-ray analysis).

As a portion of a larger study on the fate of hazardous contaminants in the Hamilton STP, composite samples were collected from the effluent on several occasions between September 1982 and May 1983 by the Water and Wastewater Management Section. These were analyzed

for heavy metals, PCB's, pesticides and a series of toxic organic compounds. Heavy metal results are integrated with the results of this study; organic contaminant results are being reported separately.

Effluent limitations are set out in the MOE publication "Guidelines for The Design of Sewage Treatment Works" (MOE 1980) for conventional parameters such as BOD, suspended solids, total phosphorus and ammonia. However, these are not dealt with here. Sewage treatment plant effluent standards for other pollutant parameters are not established.

4.2 Trace Contaminants in Hamilton Harbour

Water samples were collected from 6 sampling stations in Hamilton Harbour (Figure 1) approximately monthly from May to November, 1982. At the deep water locations (4, 258, 270) samples were collected at 0.2 and 6 m from surface and 1 m from bottom, while at the other locations, samples were collected at 0.2 m from surface and 1 m from bottom. All samples were analyzed in duplicate for Cu, Ni, Zn, Cd, Pb, Fe and Mn, and singly for Hg, As and cyanide. Surface samples only were analyzed for PCB's and pesticides. On several occasions, surface and bottom samples from station 258 were partitioned into dissolved and particulate fractions using a boat-mounted centrifuge. The centrifuged effluent was analyzed for the above heavy metals; the residues were partitioned into the five fractions previously mentioned for STP effluent residues.

Sediment samples were collected by Shipek dredge in October 1982 from 20 locations (Figure 1). These were analyzed for PCB's and organochlorine pesticides, and samples from 6 locations (2, 20, 256, 258, 262 and 268) were also analyzed for polynuclear aromatic hydrocarbons. The latter locations were selected for proximity to suspected discharge points and as a deep depositional zone.

Sediment cores were also collected at 6 locations in June 1982 by K. R. Lum. Several sections from each core were subjected to heavy metal extraction.

5.0 RESULTS AND DISCUSSION

5.1 PCB's and Organochlorine Pesticides

5.1.1 Organic Contaminant Loadings to Hamilton Harbour

Results for PCB's and organochlorine pesticides have been summarized in Tables 1 and 2 for the Hamilton and Burlington STP final effluents, and in Tables 3 and 4 for harbour water and sediments. In no case was a substance detected in 100% of samples; means and standard errors were calculated using a value of one-half the minimum detection limit where the result was below detection.

In both the Hamilton and Burlington STP effluents, the most consistently found substances were the hexachlorocyclohexanes (BHC's) and hexachlorobenzene (HCB). These were found with similar frequencies at both STP's, although the week-to-week range in concentrations was large, particularly with HCB. Mirex and PCB's were exceedingly variable. Although these were detected in less than one-half of the samples, their concentrations ranged as high as 200 (PCB's) or 250 (mirex) ng/L. These were detected more frequently in the Hamilton STP effluent than in the Burlington STP effluent, as might be expected for an STP which receives large quantities of industrial waste. Several other compounds including the chlordanes and DDT metabolites were occasionally detected (<30% of the time).

Pesticide concentrations in the Burlington STP in 1983 were considerably lower than those in 1982, as was the number of compounds found. In Hamilton, only the BHC's, PCB and HCB were found in December 1982 - January 1983, at similar concentrations to those in Table 1. The lower concentrations probably represent a seasonal change rather than a trend.

In 1974, a PCB concentration of 300 ng/L was measured in the Hamilton STP effluent during a one-week study of PCB removal in wastewater treatment (Shannon et al. 1976). This was higher than the 1982-83 maximum, and suggests a possible decreasing trend concommitant with reduced PCB usage. This is difficult to confirm, however, as analytical capabilities have improved over the years (e.g. detection limit lowered from 100 to 20 ng/L). At that time, Hamilton had one of the highest PCB effluent concentrations in Ontario, with only three locations higher on the basis of single samples (Shannon et al, 1976). No other comparison figures were available. The only other measurement at Hamilton (1979) indicated 870 ng/L, a single sample of obviously no use trend estimation.

5.1.2 Organic Contaminants in Hamilton Harbour

5.1.2.1 Surface Water

PCB-pesticide results in Hamilton Harbour surface water (Table 3) are consistent with the STP effluent results, with the BHC's and HCB being most frequently found ($\geq$25% of the time). α-BHC was most frequently found (92% of the time), and was very evenly distributed seasonally and spatially. γ-BHC was less regular, being found at station 268 (Windermere Basin; Hamilton STP) once at 59 ng/L and twice at 31 ng/L. These are in the similar range as effluent samples, but do not correlate temporally with any effluent samples. This fact is not surprising because of the large day-to-day variation in the Hamilton STP for this parameter. Excluding station 268, the harbour-wide mean for γ-BHC would be 4 ng/L.

The data for α-BHC indicate that the sewage treatment plants are not the main sources of this compound to Hamilton Harbour. Indeed, α-BHC is almost universally detected in Lake Ontario waters. It was found at a concentration of 3 to 4 ng/L in 5 out of 8 water samples analyzed in 1982 from the Burlington and Hamilton water

intakes, the only pesticide other than mirex to be detected at these locations. Kuntz and Warry (1983) found α-BHC in 100% of 75 water samples at Niagara-on-the-Lake in 1980-81, with an average concentration of 10 ng/L. Kauss (1983) also found α-BHC in most Niagara River water samples at an average concentration of 4 ng/L and suggested there was no local source of this compound because of its uniformity throughout the river system. Results obtained here indicate the same is true for Hamilton Harbour.

Only a very limited comparison of PCB-pesticide data with earlier (1975) results is possible. The only compound previously observed with any regularity, endosulfan I, was not found at all in the harbour water or sediments. Lindane (γ-BHC) and PCB's were analyzed for but not detected in 1975; they were found in 69 and 14% of the 1982 samples, respectively. All occurrences of PCB's in 1982 were at stations 20 and 268, which were not sampled in 1975, thus the results are consistent and do not indicate a worsening problem. However, γ-BHC was found at the four major stations two-thirds of the time in 1982 at an average of 4 ng/L. It is not known whether this is a result of improved analytical capability or is a new contamination. This compound was also generally present in the Niagara River (Kuntz and Warry 1983; Kauss 1983), though it was not found in the Burlington or Hamilton water works intakes in 1982. The other BHC's and HCB were not determined in 1975. Other compounds were present too infrequently to warrant a comparison.

5.1.2.2 Sediments

The distribution of PCB's in Hamilton Harbour sediment samples is shown in Figure 2. As in previous years, concentrations varied widely from one location to another. However, no correlation exists between spatial patterns found in different years. MOE guidelines for open water disposal of dredge spoils specify 50 ng/g as an acceptable concentration for PCB's (MOE 1976). This level is used as an indication of a "safe" level of contamination based on elutriate tests, and does not imply any intention to remove contaminated sediments. Although most of the highest concentrations (>500 ng/g) were found in the deepest areas and

along the industrial shoreline, the highest result (1270 ng/g) occurred at station 257 on the north shore, an area with historically low concentrations of most pollutants. Conversely, station 268 at the outlet of Windermere Basin was below detection limits. The laboratory precision in PCB analysis is about 10%; however, variations of an order of magnitude have been known to occur within a few metres in sediments (G. Rees pers. comm.). The reason for the apparently random variations in PCB levels in Hamilton Harbour sediments is presently unknown.

The most frequently occurring pesticides were α- and ɣ-chlordane and α-BHC which were found in one-half to two-thirds of all samples. HCB op-DDT, pp-DDE and β-BHC were found in 15 to 25% of the samples. No regular spatial distribution existed for any of these pesticides. This represents a possible increase in detection frequencies of the chlordanes and BHC's, and decrease for DDT metabolites from previous samples, but th data are too irregular to draw any firm conclusions.

Six sediment samples representative of the industrial shoreline and deep water location (258) were analyzed for PAH's in 1982. Summary results are given in Table 5. In all cases the maximum concentration was found at station 262 (Randle's Reef), and minimum concentration at station 20 (southeast harbour). For most compounds the order of stations from the highest PAH concentrations to the lowest was 262>2>258>268>256>20. Evidently the steel companies are the major source of PAH's, and the Hamilton STP a minor, but significant source.

The minimum PAH concentrations observed in Hamilton Harbour sediments were similar to those observed by Onuska et al. (1983) for total PAH at locations in Lake Ontario affected by sediment from the Niagara River, and up to 2 orders of magnitude higher than a mid-lake location. Maximum concentrations are higher by a further factor of 4 to 10. Average concentrations are also about 2 orders of magnitude higher than the highest Detroit River surficial sediment PAH concentration (33 ng/g) observed by Kaiser et al. (1985). The highest PAH concentrations in this study were found at locations closest to the steel mills. This was

reasonable as the highest effluent concentrations (up to 20 ug/L) of PAHs were detected in the steel mill effluents, compared to the Hamilton STP effluent (MOE unpublished data).

5.2 Heavy Metals

5.2.1 Heavy Metal Contaminant Loadings to Hamilton Harbour

Weekly heavy metal loadings from each STP were calculated by multiplying the metal concentrations by the weekly average flow as calculated from daily flow data provided by the STP's. Standard deviations of weekly flow means were 5 to 10% of the means in Burlington and 7 to 20% of the means in Hamilton for most survey weeks.

Detection limits obtained during this survey were variable and generally higher than the limits obtained for analysis of surface water samples; lower detection limits were generally obtained during analysis of the sequential (half-hourly) samples and the winter 1983 Burlington samples.

Average heavy metal concentrations and loadings over the various study periods are summarized in Tables 6 and 7. Included in Table 7 are loadings from heavy metal data provided by K.W.A. Ho, Water and Wastewater Management Section, and, for comparison, 1977 loading data (MOE, 1985). As most of the cadmium, chromium and lead results from both STP's, and nickel from the Burlington STP in 1982 were specified as "less than", upper limits for the loadings of these parameters are specified. Suspended metal loadings in 1982 were calculated by multiplying the total metal concentration in the centrifuge residue by the suspended solids loading on the nearest sample date. The total suspended metal concentrations as obtained by K. Lum of CCIW are summarized in Tables 8 and 9. These loadings should only be regarded as approximate since the centrifuging was not always done on the same day as the composite sample was taken, and did not represent the entire 24-hour interval of the composite sample. Nonetheless, the suspended metal loadings from the Hamilton STP were generally compatible with the total and dissolved (centrifuged or filtered) metal loadings reported in Table

They both reveal that most metals are largely in the dissolved form, except for iron and chromium, which appear to be mostly particulate. Similar partitioning seems to occur at Burlington.

On one occasion each STP exhibited a very high suspended solids concentration. Samples were taken July 8, 1982 at Hamilton (loading 53700 kg/day) and September 1, 1982 at Burlington (loading 4800 kg/day). They do not correlate with any unusual conditions such as storm runoff; however, the problem may be a result of errors in analysis or sampling. They were omitted from calculations of the average suspended solids and suspended heavy metals loadings calculations in Table 7.

Compared to 1977 data, the 1982-83 results show decreases in loadings for copper, zinc and chromium, and probably for cadmium and lead at the Hamilton STP. Atkins and Hawley (1978), however, quoted a lower copper concentration for the Hamilton STP (0.02 mg/L). As this was for a single 4-hour composite sample, no conclusion about trend can be drawn because of the variability in concentration as mentioned elsewhere. Other metals showed similar loadings in both years. At Burlington, loadings have in general been unchanged since 1977 except for iron which shows a definite increase, and copper, which shows a possible increase. The decreases in loading from the Hamilton STP presumably indicate reductions in contributions from the industrial wastes input to the plant. The increased iron loading from the Burlington STP is due to the use of ferric chloride for phosphorus removal which started in early 1976 (the 1977 loading estimate was computed using a 1975 concentration measurement). The increased copper loading from the Burlington STP is negligible compared to the total loadings of this metal to the harbour (MOE 1985). Copper loadings from both STP's and industries is of some concern, however, as this metal is consistently above the harbour Objective (see section on metals in the water column).

5.2.1.1 Weekly variations in loadings

Large week-to-week variations in the loadings of most metals were found, with maximum values frequently several times those of minimum values. These ranges are reflected in the standard deviations given in Table 7. Regression analysis was used to determine whether these variations were correlated. In Hamilton, zinc, iron and copper were correlated ($P<0.01$). This relationship (Figure 3) is obviously due to the common industrial source of these metals. Nickel and manganese were also correlated ($P<0.05$), but not to the other metals. Flow peaked with several rainfall events in June and August, but metal loadings were not correlated with these peak flows.

Several pairs of metals at Burlington showed minor correlations ($P<0.05$). However, they were not consistent between the summer and winter, and are thus considered unimportant. Variations in flow during the winter-spring period reflected a rainfall event in early February and spring runoff plus rainfall between late March and mid-April, but only cadmium ($P<0.05$) showed any significant relationship to runoff-induced flow.

5.2.1.2 Short-term variations in heavy metal concentrations and loadings

Grab samples were collected at half-hourly intervals using automatic samplers at both STP's during dry weather on July 15, and again under runoff on August 19-20. Beause of sampler malfunction, no runoff samples were obtained from the Burlington STP.

Hourly flow data indicated almost constant flows of $270 \pm 10 \times 10^3$ m^3/d at Hamilton and $90 \pm 10 \times 10^3$ m^3/d at Burlington during the dry weather period. Both plants showed diurnal variations in flow with minima during the early morning hours, but this was outside the monitored intervals. During the runoff period, 8 mm of rain fell at the rain gauge location between 2300 h on August 29 and 0400 h on August 20. At the Hamilton STP, constant flow occurred until 0100 h on August 20,

followed by an increase to a peak of 410 x 10^3 m^3/d at 0400 h August 20. The flow had only subsided slightly to 400 x 10^3 m^3/d at the end of sample collection (0530 h), with most of the decrease occurring in the next 5 h. Thus most of the measured interval represented pre-runoff conditions and only part of the runoff period was sampled.

Average heavy metal concentrations obtained during the sequential sampling periods are compared to weekly average data in Table 6. Detection limits for several metals were lower for the sequential samples than for the 1982 weekly composites. During the runoff period, all metals but Ni and Cd were significantly (t-test, $P<0.01$) higher than in the dry weather interval at Hamilton; this included samples obtained before the commencement of runoff. Cd was higher at $P<0.05$. For most of the metals, however, the values represented by both sequential series were within the range (where properly defined) of observed weekly concentrations, i.e. the differences between the two time series are within normal variations. Pre-runoff values for Cr, Pb and Fe were near the maximum observed weekly values. However, for Cd, weekly values were almost always "less than", but sequential values were several times higher, at 9 to 12 ug/L. Thus results for this metal were not compatible, and suggest contamination of the automatic sampler used for collecting sequential samples or some unknown mechanisms removing Cd from the composite samples.

Regression analysis was used to determine the relations between metal variations within each sampling period. At Hamilton, nearly all pairs of metals exhibited dependent relationships ($P<0.01$), except for Cd in both periods and Mn in the dry period. This agrees with the common industrial input source of most metals and also enhances the suggestion of contamination problems with Cd. Time series of Cu, Ni and Zn during the runoff period are shown in Figures 4a-4c. The metals show a "first-flush" effect of maximum concentration at 0200 or 0230 h on August 20 as the runoff commences to flow through the plant, followed by a minimum concentration 2 h later at peak flow rate.

The effect is shown by all metals except Cd and indicates some input being washed through from storm and combined sewers (strongest at the beginning of runoff and diluted later with cleaner water at peak flow). Other variations before commencement of runoff occurred to some extent with all metals and likely represent temporal loading variations. Similar conditions were seen in the dry weather time series from Hamilton.

Because of the primarily residental input, the metal loadings at Burlington are not expected to be so highly interdependent. Nevertheless, some correlations were significant ($P<0.02$). Typical variations with time (Figures 5a-5b) exhibit correlations which are statistically insignificant when compared to Hamilton data.

5.2.1.3 Comparison with other STP's

Data compiled by Environment Canada for average trace metal concentrations in 20 Ontario sewage treatment plants indicate above average effluent quality but only average removal efficiencies for the Hamilton STP (Canviro 1985). Influent concentrations for all metals with the exception of Zn fall below the Ontario mean; however, removal efficiencies for this metal and Ni are normal. All other removal efficiencies are at or near the Ontario average. This contrasts data reported by Atkins and Hawley (1978) in which influent heavy metal loadings from industries to the Hamilton STP were higher than any other studied STP in Ontario, yet effluent levels were only slightly above average. This may be attributed to good metal removal efficiency at the Hamilton STP relative to others; however, sample variances would be necessary to verify this hypothesis.
The concentrations of Cu, Zn, Cd, Pb and Fe are not significantly lower in the Burlington STP effluent than in the Hamilton STP effluent (Table 6.) The data obtained here indicate that the heavy metal concentrations from the Burlington Skyway plant are similar to or better than the average values for the plants and parameters studied.

5.2.1.4 Electron microscopy analysis of particulates from Hamilton STP

Four samples of particulate material were collected August 11, 1982 on polycarbonate membrane filters. Ten particles from each filter were examined by SEM/EDXRA (Scanning electron microscope/energy dispersive X-ray analysis) by the Electron Microscopy Unit, Laboratory Services Branch. Figure 6 shows a histogram of relative abundances of the elements found. The particles analyzed showed elemental compositions typical of the earth's crust, with Si, Ca, Al, Fe and P being the five most commonly found elements. Only Fe and P suggest the origin of the particles. Most metals emphasized in this report were found rarely or not at all. Although this goes along with the suggestion (Table 7) that most metals were predominantly dissolved, it suggests that this analytical technique is presently of very limited utility in characterizing particulate matter from STP's. However, it did suggest several other heavy metals such as Sc, Ti, V, Zr and Mo which may warrant future attention.

5.2.2. Trace Metal Contaminants in Hamilton Harbour

Trace heavy metal concentrations were determined on unfiltered water samples taken from 3 depths at station 4, 258 and 270 and 2 depths at stations 20, 252 and 268. Samples were collected on six occasions and analyzed for Cu, Ni, Zn, Cr, Pb, Fe and Mn; use of duplicate samples allowed a check of sampling and analytical variability as well as permitting the determination of interaction effects in an analysis of variance. Single samples only were analyzed for Hg, As and cyanide. In all cases, cyanide was below the detection limit of 5 ug/L; this parameter is thus not discussed further. Provincial Water Quality Objectives as outlined in the MOE Water Management "Blue Book" are included with heavy metal data at the conclusion of Table 11.

On each sampling date, one or two field blanks were taken by filling the sampler with distilled water on board the sampling vessel, and emptying into bottles for analysis for the same heavy metals. Except for two iron analyses, all blanks recorded below detection limits. The two exceptions were only a few percent of average iron levels and considerably below sampling variability. It was thus concluded that no contamination occurred during the heavy metal sampling in the water column. Such was not the case for STP effluent sampling (Sec. 5.2.1.2).

The average relative difference between the two duplicate samples obtained at each station was compared. It was found that the average variability for most metals was about 20%; however, the variability for lead and iron was 45 and 30%, respectively. Omitting bottom samples from the averaging reduced the iron variability to 25% but had no effect on all other metals. The high variability for lead was not surprising, as a large number of samples were below the detection limit and most averages were less than twice the detection limit. A possible reason for the high variability associated with iron could be variable amounts of suspended material in the duplicate samples (especially in bottom samples) as this metal was largely in the particulate phase (all centrifuge effluent samples had less than 0.05 mg/L Fe). High variability was also noted in the partitioning of samples into particulate and dissolved, as noted elsewhere.

Three-way analysis of variance (station/depth/date) was performed on the results for Cu, Ni, Zn, Fe and Mn. The other metals had large numbers of results below detection limits and the analysis was thus considered not applicable. Data were tested for normal distribution using the Kolmogorov-Smirnov test; it was found that the best distribution characteristics were obtained by transformation of Cu and Ni to square roots and the log transformation of other parameters.

Multiple-factor analysis of variance is complicated by the existence of interactions between the various factors. As replicate observations were performed on each station/date/depth combination, both two-way and three-way interaction terms can be computed. Both the

main effects and the interaction were tested for significance, although Sokal and Rohlf (1969) state that it is usually not of interest to test for the main effects when the interaction terms are significant. For most parameters, the interaction terms were not significant; even when they were, it was found that the main effects generally accounted for most of the variance. All analyses of variance were performed using the SAS Statistical Package (Helwig and Council, 1979).

Shallow water at two stations precluded sampling below 6 m and as a result, the data was subdivided into two groups based on samples obtained: (a) stations 4, 258 and 270 at surface, 6m and bottom; and (b) stations 4, 20, 252, 258 and 270 at surface and 6m only. The results obtained are given in Table 10.

In general, the greatest variations were with respect to sampling date, followed next by station. The five-station group gave greater variation with respect to station than the three-station model, as could be expected since metal concentrations are higher in the southeast part of the harbour (station 20). This group gave a large number of station-date interactions as well, presumably indicating that stations 20 and 252 are more variable with respect to dates than the other stations. Indeed, the heavy metal loadings from the STP's are quite variable with respect to time, as discussed elsewhere in this report. Interaction terms are generally significant only with zinc and manganese (plus the three-way interaction for nickel). Variation with depth was significant only for manganese.

The variations of manganese with depth, and its interactions with time and station are related to the release of dissolved manganese from the sediment at the lower redox potentials which develop as a result of the anoxic or near-anoxic conditions at the sediment-water interface. On May 22, duplicate results at the bottom of station 258 were 0.10 and 0.04 mg/L; these increased gradually throughout summer to 0.88 and 0.82 mg/L on October 8 (bottom D.O. = 0.7 mg/L). Following overturn, the bottom concentration was 0.046 and 0.057 mg/L on November 26. A similar increase occurred at station 4 but not at the shallower station 270 (thus the interactions with station).

A more complete experiment on the time-depth variation of iron and manganese was performed in 1979, but has not been reported. The purpose of this experiment was to test the extent of reduction at the sediment-water interface, and its influence on heavy metal chemistry. Weekly samples were collected from July to October at depths of 0.2, 6, 12, 16 and 20m at station 258 and analyzed for the above metals. Depth-time distributions are plotted in Figure 7. Although the iron data indicated no release from the sediments except perhaps briefly in late August, manganese was gradually released from the bottom sediments, with the concentration reaching 1.2 mg/L in early October. The increased Mn concentrations were confined to the lower hypolimnion. After overturn, Mn concentrations rapidly dropped below 0.1 mg/L in the entire water column as oxidizing conditions reappeared.

The behavior of both metals may be explained by the relative electrochemical potentials of the redox couples Fe(II)-Fe(III) and Mn(II)-Mn(IV) (Stumm and Morgan 1970). After dissolved oxygen has been consumed, nitrate (NO_3^-) and nitrite (NO_2^-) are reduced, with MnO_2 reduction occurring at about the same redox potential. This is followed by reduction of Fe^{3+}, and at sufficiently negative redox potentials, by fermentation (CH_4 formation) and reduction of SO_4 to $S^=$. In real systems containing organic matter such as Hamilton Harbour, many redox couples exist simultaneously, i.e. a mixed potential (Stumm and Morgan 1970). Inflow of oxygenated water from Lake Ontario also helps to stabilize the redox potential at a value sufficient to allow dentrification (MOE 1981, 1985) and manganese reduction but not low enough to allow iron reduction.

The importance of these factors in managing the water quality of Hamilton Harbour lies in the fact that, if complete depletion of NO_3^- from the hypolimnion occurred through accelerated reduction, Fe^{2+} (and consequently phosphate) would be liberated from the sediments. These reactions could also occur if nitrate loadings were

reduced without corresponding reductions in organic carbon and phosphorus loadings. Thus increased concentrations of phosphate in the water column, and a potential for increased phytoplankton growth could occur, a situation clearly to be avoided. This effect of nitrate concentration on phosphorus reduction from the sediment was also observed recently in several Danish lakes by Anderson (1982), who found that release of phosphorus from the sediments to the anoxic hypolimnion occurred only if nitrate-N concentrations were below about 0.5 mg/L.

5.2.2.1 Average heavy metal concentrations and comparison with Objectives

Although analysis of variance indicated that the largest proportion of variance was accounted for by between-date-variations, inspection of cruise averages indicated that for most parameters seasonal variations were random. An exception was manganese, as already discussed. Consequently, the data were summarized by station. Table 11 gives summary statistics by station for each parameter. Included are percent of samples exceeding Provincial Water Quality Objectives. In all cases except manganese and mercury, station 268 (nearest the Hamilton STP) has the largest average concentrations and percentages of Objective exceedances; station 20 is next highest in most cases. The latter is not surprising considering the distinct zonation of this station according to most water quality parameters (MOE 1985). Higher manganese averages (and standard deviations) at stations 4 and 258 reflect the increased bottom water concentrations at these stations as already discussed.

The parameter with the largest proportion of Provincial Water Quality Objective infractions was copper, which exceeded Objective levels 66% of the time as a whole, and 100% of the time at station 268. This was followed by iron (29%), zinc (25%), cadmium (17%), nickel (3%), mercury (2%) and lead (1%). Arsenic did not violate Objectives at any time. These findings may be contrasted with the limited data of 1975-80, for which it was found that zinc nearly always

exceeded Objectives, while iron exceeded Objectives most of the time at stations 4 and 20, and occasionally elsewhere (MOE 1985). The results indicate a dramatic reduction in zinc concentrations from 1977-80 averages of 42-52 ug/L at station 258 to the 1982 average of 19 ug/L. Although iron still exceeds Objective levels most of the time at station 20, its average concentration has dropped from 0.80 $\pm$ 0.64 mg/L in 1979 to 0.41$\pm$ 0.14 mg/L in 1982. The proportion of Objective violations, and average levels elsewhere in the harbour have both dropped since 1979.

The only other heavy metal data available at a low detection limit, with which the 1982 data may reasonably be compared, is a single 13-station survey in October 1980. Harbourwide means and standard deviations, excluding stations 20 and 268 (high concentration areas) are compared in Table 12. These results also show the decreases in iron and zinc already referred to, and in addition show decreases in copper and manganese concentrations. As no changes in analytical procedures have occurred in this time interval, and the observed decreases are far greater than the magnitude of analytical error (B. Loescher pers. comm.), these changes represent definite improvements in water quality. Cadmium, lead and nickel showed no significant changes during this time interval.

Except for the single survey in 1980, these data are the first indication of widespread exceedences of the PWQO for copper in Hamilton Harbour. Other Lake Ontario surveys in recent years, however, do indicate appreciable fractions of parameters above Objective level. For example, at "background" locations in Lake Ontario 3 to 5 km east of the Burlington Ship Canal, copper concentrations of 2 to 9 ug/L with an average of 4 ug/L and about 20% above Objective level were found in 1982 (MOE 1986). In the Toronto Waterfront, average inner and outer harbour values were 4 ug/L with 23% above Objective and 15% above Objective in the Toronto nearshore region in 1981 (Griffiths 1983). Although a significant improvement has occurred in the past few years, there is definite evidence that a significant pollution problem still exists with regard to copper, not only in Hamilton Harbour but in nearshore areas of Lake Ontario as well.

5.2.2.2 Partitioning of particulate and dissolved metals

On three dates during 1982, water from the surface and 20m depth of station 258 was passed through a continuous-flow centrifuge on board the sampling vessel until enough suspended solids were collected for a heavy metal speciation analysis by K. Lum of CCIW. Only on June 19 was the centrifuging done on the same date as the regular sampling collection. No centrifuging was done in May; the date for the other centrifuging varied by as much as six days from the regular sample collection.

Samples of the centrifuge effluent were analyzed in order to estimate the fraction of each metal in the dissolved (or finely particulate) phase. As most results for Cd and Pb were at or below detection limit (see table 11), no meaningful results were obtained for these metals. In addition, Cu and Ni frequently showed a higher concentration in the centrifuge effluent than in the total sample, i.e. apparently more than 100% dissolved. This may have occurred because either (a) the results were often close to detection limits; or (b) the samples were not collected on the same day and may have been subject to small-scale variability (the variability was often similar to the differences between the duplicate samples). On an average basis, Cu and Ni were essentially all in the dissolved phase.

Only for zinc, iron and manganese was a significant fraction of particulate material found. Zinc was 50 to 80% particulate at the surface and 20 to 40% particulate at the bottom. Bottom manganese was 95% particulate on June 19 and 25% particulate on August 29. This change is as expected, due to the accumulation of dissolved manganese under summer anoxia (Figure 7). Surface manganese varied from 65 to 95% particulate with no seasonal trend. Iron was about 90% particulate at the surface but varied widely from 20 to 93% at the bottom, also without seasonal trend. This variation was not consistent with what would be

expected for reduction of Fe(III) to Fe(II) as summer progresses, and its cause is unknown. The overall variability as observed here, plus the problems stated above with Cu and Ni indicate that all results are only very approximate and must be used with caution.

5.2.2.3 Suspended sediment analyses

The suspended sediment samples collected at station 258 and from the STP effluents were analyzed for heavy metals by K. Lum of CCIW. Total heavy metal results are summarized in Table 13. In all cases, surface suspended sediment heavy metal concentrations are considerably lower than bottom suspended sediment metal concentrations. The results are compared with results of the uppermost layer of a sediment core collected in 1980. For most metals, these values are within the range of results shown for bottom suspended sediments. For Fe and Zn, however, the suspended sediments show a lower concentration than core values, suggesting a reduction of sedimentary input. For Mn, the bottom suspended sediments show a considerably higher concentration than the core value. This may have been caused by air oxidation of Mn^{2+} during centrifugation.

5.2.2.4 Heavy metal speciation in particulates

Previous work on the partitioning of heavy metals in Hamilton Harbour suspended sediments was done by R. MacDonald, K. Lum and co-workers (McIsaac et al. 1981). They found that the most important chemical phase in the suspended material was the Fe-Mn oxides for most metals. Residual forms predominated for several metals while organically bound predominated for Cu only. Although they did not predominate, the exchangeable and surface oxide-carbonate bound forms contained significant proportions of several metals.

The results of partitioning the heavy metal content of suspended sediments from station 258 and the STP's are discussed in detail by K. Lum (report in preparation) and will only be briefly summarized here. They will be compared with the previous partitioning

data (McIsaac et al. 1981) as well as several other studies in which the chemical partitioning of heavy metals was studied. The latter include Gibbs (1977), who studied two unpolluted rivers, the Yukon and Amazon, and Tessier et al. (1980), who studied two rivers in Quebec which included locations influenced by municipal sewage and mine drainage effluents.

The dominant phases observed from the various input and harbour locations are summarized qualitatively in Table 14. Where more than one phase is given, it indicates that different phases dominated on different dates. Occasionally, two or three phases contained similar concentrations. Although not included in Table 14, other phases generally comprise appreciable fractions of the total content for some metals.

In no case did the exchangeable phase predominate. In fact, its contribution from the STP effluents was never more than a few percent of the total and was frequently below detection. At station 258, it sometimes comprised 10-25% of the total Cu, Ni, Mn and Zn. Although present in nearly all samples, the surface oxide-carbonate phase only occasionally dominated (most often for manganese). The other three phases (Fe-Mn oxides, organic plus sulphide, and residual) were all of great importance in determining metal transport and are discussed below.

In the harbour, residual phases dominated the speciations of cobalt and iron. Organic and residual phases co-dominated for chromium, copper and nickel, with the latter metal showing a tendency to be dominated by organic forms in the surface samples and residual forms in the bottom samples. The reducible (Fe-Mn oxide) phase dominated the speciation of zinc and bottom samples for manganese, but in surface samples for manganese, the surface oxide-carbonate phase tended to dominate. Results for lead varied from sample to sample, with Fe-Mn oxide, organic and residual phases all dominating at one time or another.

In the STP effluents, heavy metal speciation was similar to that in the harbour except that the organic phase often accounted for a higher percent of the total, becoming dominant in the case of chromium at Hamilton. Nickel speciation showed a shift towards dominance by the Fe-Mn oxide phase in several samples, although all phases contained significant amounts, and various phases dominated at one time or another in the effluents from both STP's. Undoubtedly, the sewage environments rich in iron and organic matter played a role in the observed shifts in speciation.

For the most part, the results obtain here were similar to those of McIsaac et al. (1981) in their series of samples obtained from the eastern part of Hamilton Harbour. The major difference was that the organic phase was less dominant in their samples, predominating only for copper. Although copper still exhibited the highest percentages bound to organic matter of any metal in this study, the organic phase dominated or co-dominated frequently for chromium, lead, nickel and zinc as well. The Fe-Mn oxide phase was somewhat more dominant in their samples, particularly in the cases of lead and chromium. The reason for this apparent shift from the Fe-Mn oxide phase towards the organic phase is unknown.

Compared to studies in other locations (Gibbs 1977; Tessier et al. 1980) the Hamilton Harbour samples again show a greater contribution by organic and Fe-Mn oxide phases for many metals. This was particularly true for chromium, copper and zinc, as well as for iron for which the organic phase was generally second in importance to the residual phase. The difference can be attributed to the presence of large amounts of organic matter and iron compounds in the harbour and STP effluents. Tessier et al. (1980) also found large amounts of copper associated with organic matter at contaminated locations. The observed affinity of Cu for organic matter can be supported by the fact that for most ligands copper has the highest stability constants of all the metals studied here (Stumm and Morgan 1970).

In general, this study has shown the importance of Fe-Mn oxides and organic matter in binding suspended heavy metals. These results are important in harbour management considerations, because under increased extent of hypolimnetic anoxia, metals sorbed to Fe-Mn oxides could be released to solution with consequently increased bioavailability or toxicity. Reduction of organic matter content, could on the other hand, increase the amount of available Cu, Cr and Ni if metal loadings are not also reduced. Metals in the exchangeable and surface oxide-carbonate phase (such as Mn) are the most readily available, as they equilibriate more rapidly with biological fluids than the other forms. Although an acid discharge would dissolve carbonate-bound metals, these would be reprecipitated by the harbour alkalinity.

6.0 ACKNOWLEDGEMENTS

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TABLE 1

PCB and organochlorine pesticides in Hamilton STP final effluents, 1982-83, ng/L (ppt)

(a) June 3 - Sept. 1, 1982 (14 samples)

Parameter	Mean ± SE	Max.	Min.	% of samples detected
Total PCB	43 ± 8	190	ND	50
α -BHC	5 ± 1	15	ND	71
β -BHC	4 ± 2	19	ND	43
ɣ -BHC	17 ± 7	99	ND	64
α -chlordane	< 2	4	ND	29
ɣ -chlordane	3 ± 1	10	ND	29
mirex	18 ± 9	120	ND	29
pp-DDD	< 5	15	ND	7
pp-DDE	< 5	15	ND	21
pp-DDT	< 5	10	ND	7
HCB	13 ± 9	124	ND	57

TABLE 2

PCB and Organochlorine Pesticides in Burlington STP Final Effluents, 1982-83, ng/L (ppt)

(a) May 27-Sept. 1/82 (15 samples)

Parameter	Mean ± SE	Max.	Min.	% of samples detected
Total PCB	30 ± 13	200	ND	27
α -BHC	4 ± 1	13	ND	67
β -BHC	5 ± 2	29	ND	33
ɣ -BHC	13 ± 3	44	ND	80
α -chlordane	< 2	4	ND	13
ɣ -chlordane	< 2	8	ND	13
dieldrin	< 2	4	ND	7
mirex	20 ± 20	250	ND	13
pp-DDE	< 1	3	ND	7
HCB	40 ± 20	250	ND	60
(b) Jan. 13 - Apr. 29/83 (13 samples)				
@ -BHC	3 ± 2	25	ND	62
β -BHC	<2	12	ND	8
ɣ -BHC	5 ± 2	16	ND	69
heptachlor epoxide	<1	1	ND	8
HCB	18 ± 6	57	ND	62

Note: 1. Overall arithmetic means and standard errors (S.E.) of concentrations using one-half of detection limit values (prefixed by " " where necessary)

2. ND = none detected

3. The following were not detected at any time: Heptachlor expoxide (1982 only); PCB's, chlordanes (α- and ɣ-), dieldrin, mirex, pp-DDE (1983 only); methoxychlor, endosulfan I and II, endrin, endosulfan sulphate, heptachlor, op-DDT, pp-DDT, pp-DDD (both 1982 and 1983).

TABLE 3

PCB's and organochlorine pesticides in Hamilton Harbour surface waters, 1982, ng/L

Parameter	Mean ± SE	Max.	Min.	PWQO	% of samples detected	% exceeding Objectives
Total PCB	< 20	30	ND	1	14	14
α -BHC	4 ± 0.2	6	ND	-	92	-
β -BHC	< 1	3	ND	-	14	-
ɣ -BHC	8 ± 2	59	ND	10	69	14
Endosulfan sulphate	< 4	4	ND	-	3	-
Heptachlor epoxide	< 1	1	ND	1	3	0
Oxychlordane	< 2	4	ND	-	6	-
HCB	< 1	4	ND	-	25	-

Note: 1. Overall arithmetic mean and standard error (S.E.) of concentration using one-half of detection limit values (prefixed by "<" where necessary)

2. Total number of samples = 36

3. ND = none detected

4. The following were not detected at any time: aldrin, α- and ɣ-chlordane, dieldrin, methoxychlor, endosulfan I and II, endrin, heptachlor, mirex, DDT and its metabolites.

\- Objective not set.

TABLE 4

PCB's and ORGANOCHLORINE PESTICIDES IN HAMILTON HARBOUR SEDIMENTS, OCTOBER 1982, ng/g

Parameter	Mean ± SE	Max.	Min.	% of of Samples Detected	MOE Dredging Guideline
Total PCB	440 ± 80	1270	ND	85	50
Aldrin	< 1	1	ND	5	-
α -BHC	2 ± 0.4	6	ND	50	-
β -BHC	2 ± 0.7	13	ND	15	-
α -chlordane	5 ± 1	18	ND	55	-
ɣ -chlordane	7 ± 1	20	ND	65	-
oxychlordane	< 2	8	ND	5	-
op-DDT	< 5	10	ND	15	-
pp-DDE	< 1	9	ND	25	-
HCB	< 1	4	ND	25	-

Note: 1. Overall arithmetic mean and standard error (S.E.) of concentration using one-half of detection limit values (prefixed by "<" where necessary)

2. Total number of samples = 20

3. ND = none detected

4. The following were not detected at any time: ɣ-BHC, dieldrin, methoxychlor, endosulfan I and II, endrin, heptachlor, mirex, pp-DDD, pp-DDT.

\- Guideline not set: at present, values compared to known contaminated areas for qualitative description.

TABLE 5

POLYNUCLEAR AROMATIC HYDROCARBONS IN
HAMILTON HARBOUR SEDIMENTS

1982

Compound	Range (ug/g)*
Fluoranthene	1.9 - 4.3
Perylene	1.2 - 9.7
Benzo (K) fluoranthene	1.1 - 9.0
Benzo (a) pyrene	1.2 - 11.1
Benzo (g,h,i) perylene	1.6 - 8.6
Indene (1,2,3,cd) pyrene	1.1 - 9.7

* Number of Samples = 6 (stations 2, 20, 256, 258, 262 and 268)

TABLE 6

MEAN CONCENTRATIONS OF HEAVY METALS IN EFFLUENTS
FROM THE HAMILTON AND BURLINGTON STP, 1982

	Hamilton			Burlington		
	Weekly Composites 1982	Dry Sequential 820715	Runoff Sequential 820819-20	Weekly Composites 1982	Dry Sequential 820819-20	Weekly Composites 1983
Cu	35(17)	20(4)	37(12)	39(15)	33(8)	22(12)
Ni	47(23)	47(11)	45(7)	<20	5(1)	5(1)
Zn	80(35)	60(11)	125(41)	97(30)	106(9)	93(3)
Cd	<2	8.6(2.4)	10(2)	<3	12(1)	5(3)
Cr	<30	14(6)	83(33)	<20	5(1)	4(4)
Pb	<30	6(4)	26(8)	<30	7(3)	<5(2)
Fe	800(700)	300(130)	2200(800)	900(260)	970(100)	692(304)
Mn	90(20)	80(10)	140(20)	49(31)	48(17)	74(46)

Note: All results in ug/L. Numbers in parenthesis are standard deviations.

TABLE 7

Average heavy metal loadings to Hamilton Harbour from the Hamilton and Burlington STP's, 1982-1983 (kg/d)

Location	Date		Cu	Ni	Zn	Cd	Cr	Pb	Fe	Mn	Susp. solids
Hamilton	May-Sept. 1982	(T)	9.5 (4.6)	13 (6)	21 (10)	0.5	9	7	230 (180)	24 (6)	3900 (2200)
		(S)	1.9 (1.1)	0.7 (0.8)	5.7 (4.2)	-	6.1 (3.8)	1.9 (1.2)	130 (80)	1.8 (1.9)	-
	Sept. 82-Jan. 83*	(C)	3	11	14	3	3	3	28	-	-
	1977**	(T)	18	-	86	1.3	38	10	299	33	11600
Burlington	May-Sept. 1982	(T)	2.7 (1.1)	1	7.0 (2.4)	0.2	1	2	64 (20)	3.5 (2.4)	520 (180)
		(S)	0.28 (0.08)	0.03 (0.02)	0.76 (0.24)	-	0.17 (0.09)	0.11 (0.05)	39 (21)	0.49 (0.14)	-
	Jan.-Apr. 1983	(T)	1.7 (0.4)	0.4 (0.1)	8.6 (2.1)	0.5 (0.3)	0.4 (0.4)	0.4	61 (24)	6.8 (3.9)	460 (240)
	1977**		1	-	5	-	1	-	7	5	910

Notes: Figures in parenthesis are standard deviations.
Anomalous suspended solids concentrations observed July 8, 1982 (Hamilton) and September 1, 1982 (Burlington), and anomalous heavy metal concentrations observed September 1, 1982 and April 20, 1983 (both Burlington) were not used in the averages.

(T) Total (S) Suspended (C) Centrate or filtered

* Data from K.W.A. Ho, Wastewater Treatment Section.

** Data from MOE, 1985. Burlington data used 1975 concentration estimates.

TABLE 8

Total Heavy Metal Concentrations In
Suspended Sediments from Burlington WPCP Effluent, 1982

Date	Co	Cr	Cu	Fe (mg/g)	Mn (mg/g)	Ni	Pb	Zn
June 25	15	360	480	55.6	840	51	170	1300
July 8	28	350	660	78.2	1160	49	280	2400
July 20	33	435	410	99.1	930	75	250	1400
Aug. 4	19	250	740	58.1	900	49	160	1000
Aug. 19	30	190	580	73.6	1010	23	220	1600
Sept. 1	83	200	680	94.6	8100	33	160	2300

Note: All results in ug/g unless otherwise stated.

TABLE 9

Total Heavy Metal Concentrations in
Suspended Sediments from Hamilton WPCP Effluent, 1982

Date	Co	Cr	Cu	Fe (mg/g)	Mn	Ni	Pb	Zn
June 18	8.6	1810	410	25.9	350	150	500	880
July 2	8.4	1400	400	25.0	170	80	500	1070
July 14	10.9	1790	550	32.2	330	100	540	2400
July 29	10.8	1690	360	26.6	290	130	320	850
Aug. 11	8.7	950	420	27.4	310	70	280	820
Aug. 25	22.1	1120	510	40.9	830	320	440	1780

Note: All results in ug/g unless otherwise stated.

TABLE 10

ANALYSIS OF VARIANCE, TRACE METALS
HAMILTON HARBOUR, 1982

(a) Stations 4,258,270, surface, mid-depth, bottom

Metal	Station	Date	Station * Date	Depth	Station * depth	Date * depth	Station * date * depth
Cu	NS	31.59**	NS	NS	NS	NS	NS
Ni	4.61*	24.89**	NS	NS	NS	NS	3.41**
Zn	9.62**	25.62**	2.08*	NS	3.46*	2.16*	2.26**
Fe	6.57**	3.14*	NS	NS	NS	NS	NS
Mn	5.97**	5.19**	NS	56.8**	7.14**	4.01**	2.48**
(df)	2,54	5,54	10,54	2,54	4,54	10,54	20,54

(b) Stations 4, 20, 252, 258, 270, surface and mid-depth only.

Cu	NS	33.90**	NS	NS	NS	NS	NS
Ni	43.48**	39.19**	2.16*	NS	NS	NS	3.47**
Zn	17.81**	7.84**	2.69**	NS	NS	NS	NS
Fe	34.74**	5.88**	3.68**	NS	4.70**	NS	NS
Mn	14.62**	27.12**	3.86**	10.74**	4.80**	2.64*	NS
(df)	4,60	5,60	20,60	1,60	4,60	5,60	20,60

Note: Data for Cu and Ni transformed by taking square root, and data for Zn, Fe, Mn transformed by taking logarithm, to improve distribution characteristics

Values given are F-test statistics, df = degrees of freedom
NS - not significant
* - significant at 5% level
** - significant at 1% level

TABLE 11

SUMMARY STATISTICS OF HEAVY METAL DATA
BY STATION, HAMILTON HARBOUR, 1982 (ug/L)

Station		Cu	Ni	Zn	Cd	Pb	Fe	Mn	Hg	As
4	Median	7	5	20	<0.2	4	210	52	0.04	1
	Min.	1	2	10	<0.2	<3	20	17	0.03	<1
	Max.	20	11	116	0.6	31	1000	760	0.26	3
	% below D.L.	0	0	0	69	31	0	0	44	44
	% above PWQO	56	0	17	14	3	28	-	3	.0
20	Median.	8	7	32	<0.2	6	390	59	0.08	1
	Min.	3	4	19	<0.2	<3	180	34	<.03	<1
	Max.	14	12	41	0.5	12	660	92	.25	1
	% below D.L.	0	0	0	54	25	0	0	25	25
	% above PWQO	67	0	58	21	0	75	-	8	0
252	Median	7	5	18	<0.2	4	170	39	0.10	<1
	Min.	2	<1	2	<0.2	<3	20	22	<0.03	<1
	Max.	17	10	50	0.9	11	790	91	0.16	1
	% below D.L.	0	8	0	67	42	0	0	25	50
	% above PWQO	71	0	8	25	0	8	-	0	0
258	Median	7	5	16	<0.2	4	150	47	0.07	<1
	Min.	<1	2	10	<0.2	<1	52	17	<0.03	<1
	Max.	40	17	44	0.4	10	460	880	0.21	1
	% below D.L.	6	0	0	78	53	0	0	22	67
	% above PWQO	61	0	11	14	0	11	-	3	0
268	Median	10	16	38	0.2	9	400	97	0.07	1
	Min.	6	9	21	<0.2	<3	224	52	0.04	1
	Max.	33	38	129	1.7	30	2100	120	0.20	2
	% below D.L.	0	0	0	42	8	0	0	0	0
	% above PWQO	100	23	82	32	5	68	-	0	0
270	Median	7	5	16	<0.2	2	170	43	0.06	<1
	Min.	2	1	11	<0.2	<3	70	17	<0.03	<1
	Max.	30	7	36	0.4	10	350	140	0.20	1
	% below D.L.	0	0	0	81	50	0	0	28	61
	% above PWQO	58	0	3	6	0	8	-	00	0
Detection Limit (D.L.)		1	1	1	0.2	3	3	1	0.03	1
PWQO		5	25	30	0.2	25	300	-	0.2	100

Note: All values are in ug/L.

Number of data points:
= 36 for each metal, except 18 for Hg, As at stations 4, 258, 270.
= 24 for each metal, except 12 for Hg, As at stations 20, 252, 268.

TABLE 12

COMPARISON OF HARBOUR-WIDE AVERAGES FOR
HEAVY METALS DETECTED IN SURFACE WATER 1980
(1 SURVEY) VS. 1982 (6 SURVEYS)

Parameter	1980 Mean	1980 SD	1982 Mean	1982 SD	PWQO
Cu	31	21	7	5	5
Cd	0.3	0.2	0.2	0.1	0.2
Cr	1	-	-	-	100
Pb	7	3	5	3	25
Ni	4	1	5	2	25
Mn*	73	10	39	13	#
Fe	300	60	200	130	300
Zn	46	18	20	12	30

Note: All values in ug/L.
Stations 20 and 268 were not included in the above calculation.
* surface values only, excluding also station 262 (1980).

Objective not set.

TABLE 13

Total Heavy Metal Analyses
Hamilton Harbour Suspended Sediments, 1982

Date	Location	Co	Cr	Cu	Fe (mg/g)	Mn (mg/g)	Ni	Pb	Zn
June 19	St. 258 0.2m	5.8	57	42	20.2	2.2	19	70	700
	20m	17	270	210	48.2	49.7	87	140	1500
Aug. 1	St. 258 0.2m	2.3	24	34	7.7	1.3	17	28	450
	20m	39	320	150	60.1	48.9	86	590	1440
Aug. 29	St. 258 0.2m	11	41	42	16.3	2.8	23	48	520
	20m	58	150	140	56.8	15.8	67	273	1700
1980 surface core value		15	260	190	89	3.2	66	510	5700

Note: All results in ug/g unless otherwise stated.

TABLE 14

DOMINANT PHASES FOUND IN SPECIATION
ANALYSIS OF CENTRIFUGE RESIDUES

Location	Al	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Hamilton STP	E	E	D	D	D+E	B+C	C+D+E	C+D+E	C+D
Burlington STP	E	E	E	D	E	B+C	C+D+E	C+E	C+D
Stn. 258 0.2m	E	E	D+E	D+E	E	B	D	C+D+E	C
Stn. 258 20m	E	E	C+D+E	D+E	E	C	D+E	C+D	C+D

Note: A = exchangeable
B = surface oxide-carbonate
C = bound to Fe-Mn oxides
D = organic plus sulphide
E = residual

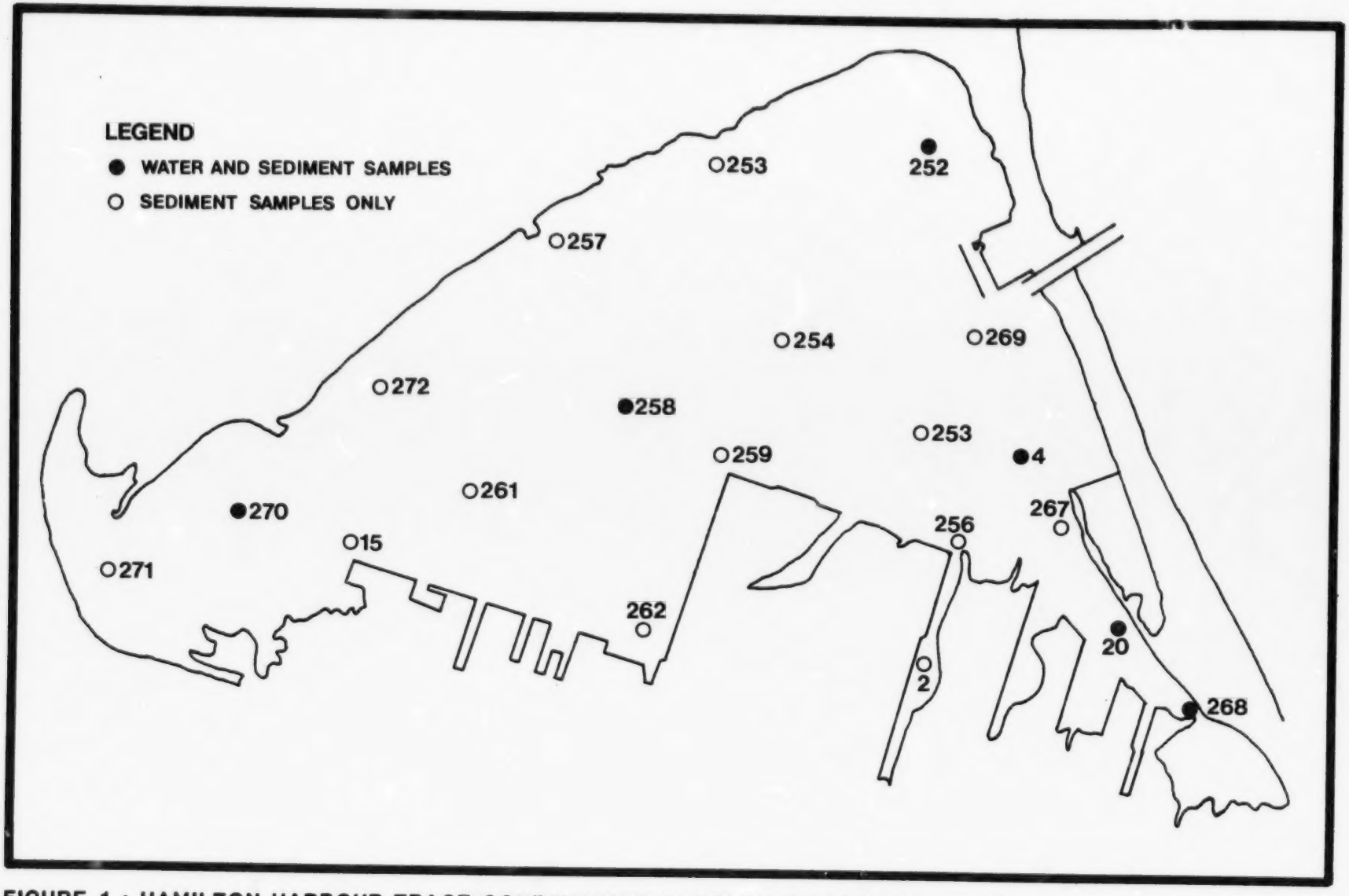

FIGURE 1 : HAMILTON HARBOUR TRACE CONTAMINANT SAMPLING LOCATIONS, 1982

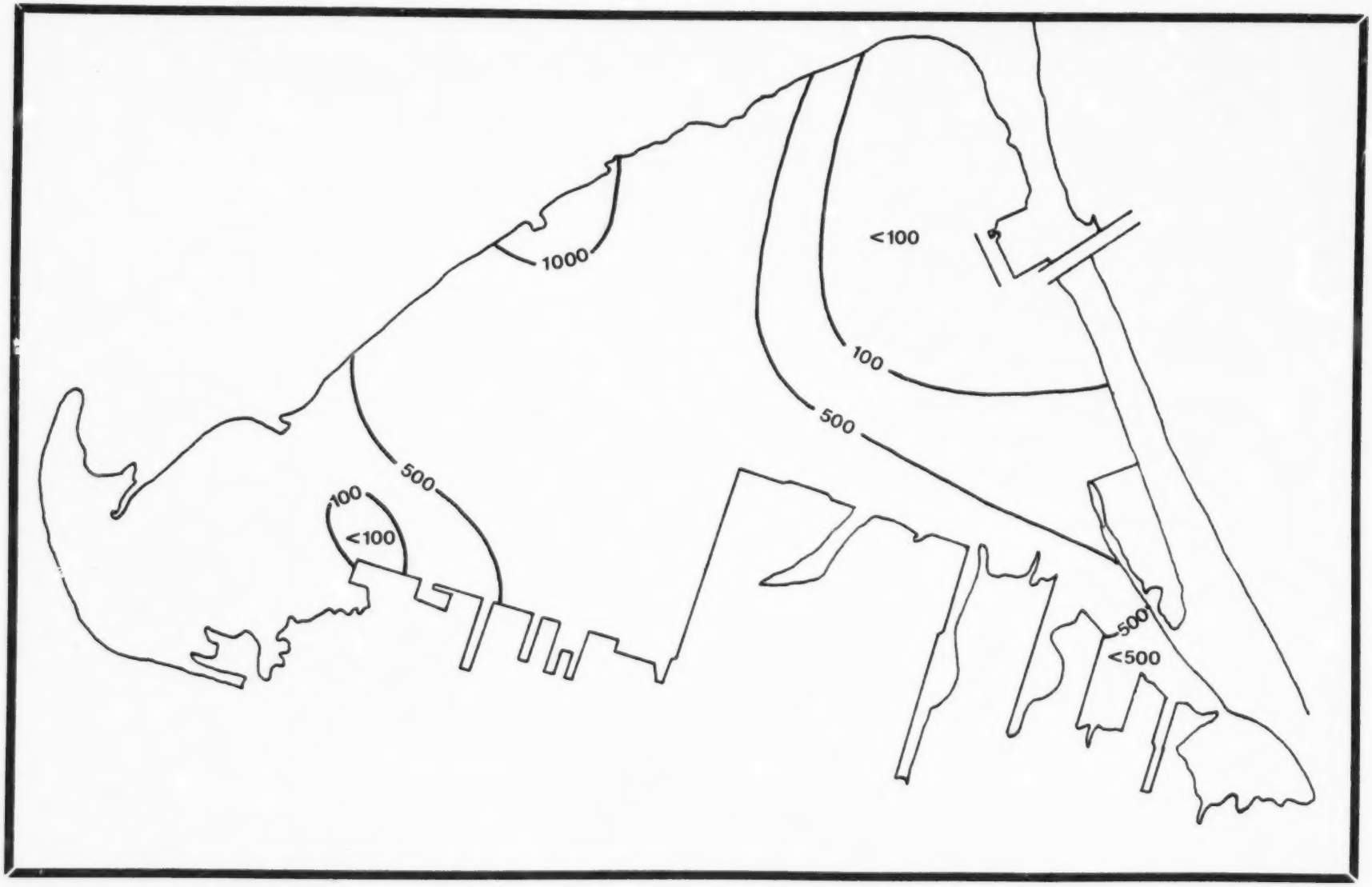

FIGURE 2 : PCB CONCENTRATIONS IN HAMILTON HARBOUR SEDIMENTS, 1982, ng/g

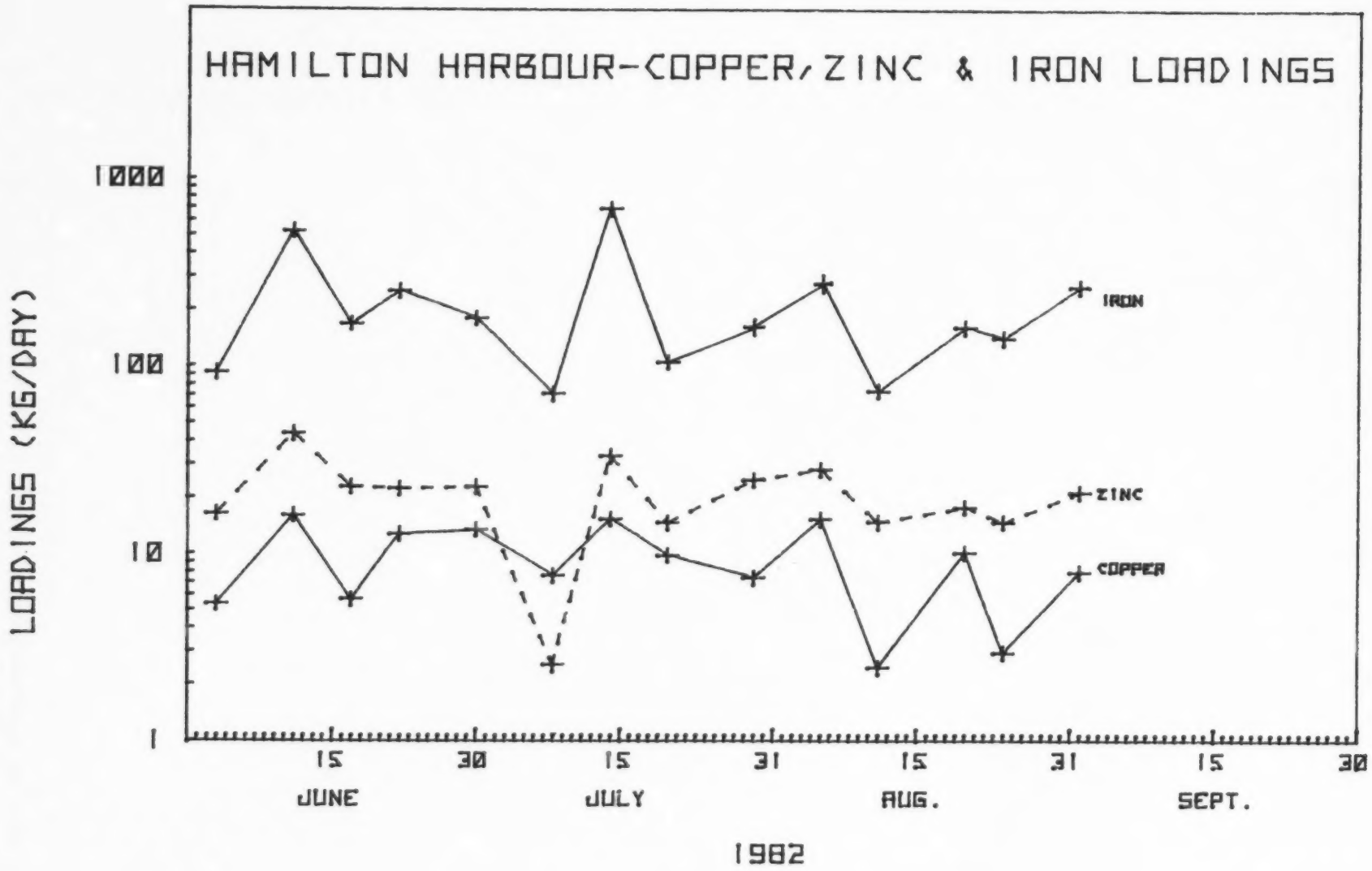

FIGURE 3 : WEEK-TO-WEEK VARIATION IN LOADINGS FROM HAMILTON STP

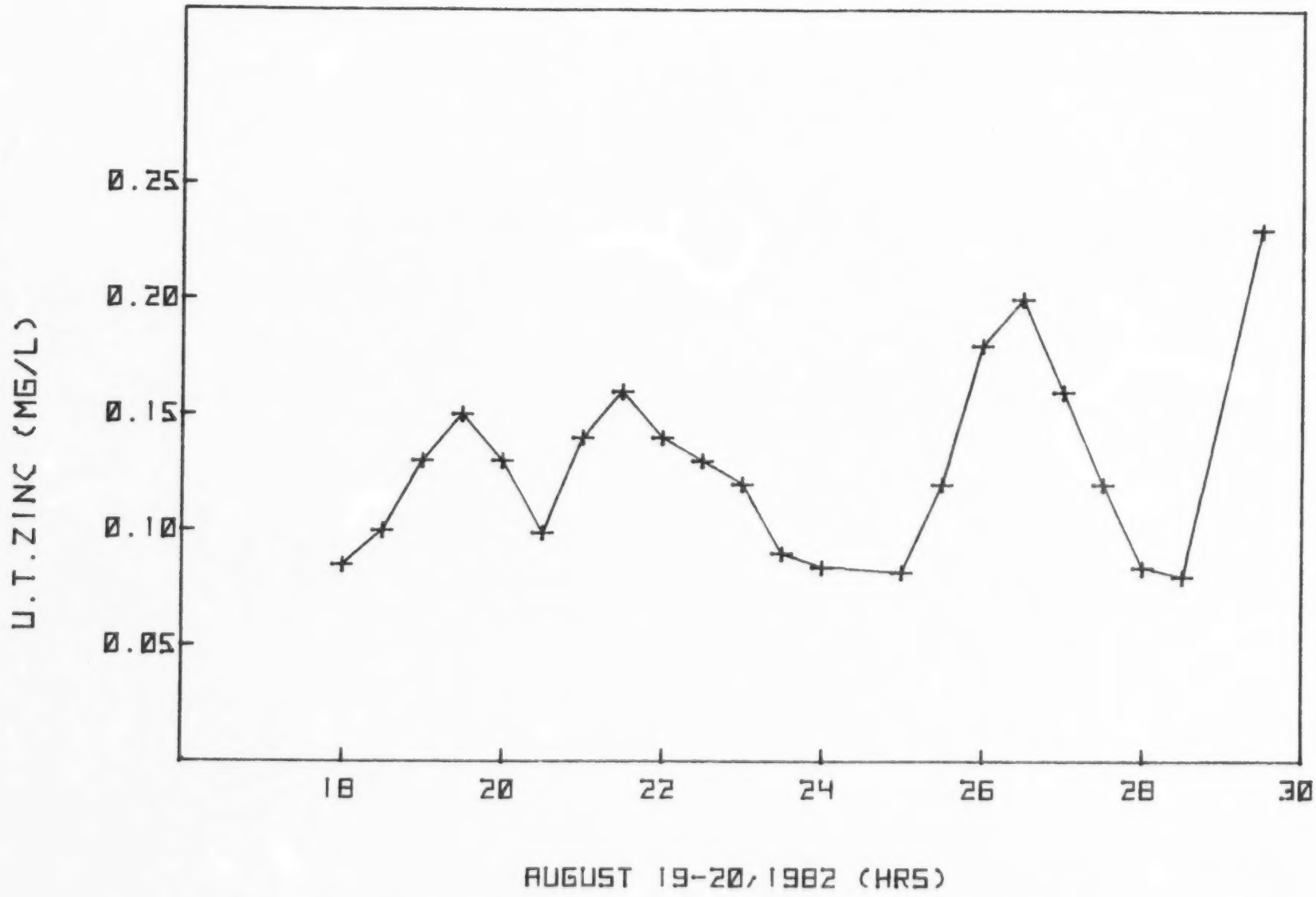

FIGURE 4a : VARIATION OF ZINC CONCENTRATION WITH TIME AT HAMILTON STP DURING RUNOFF SAMPLING PERIOD

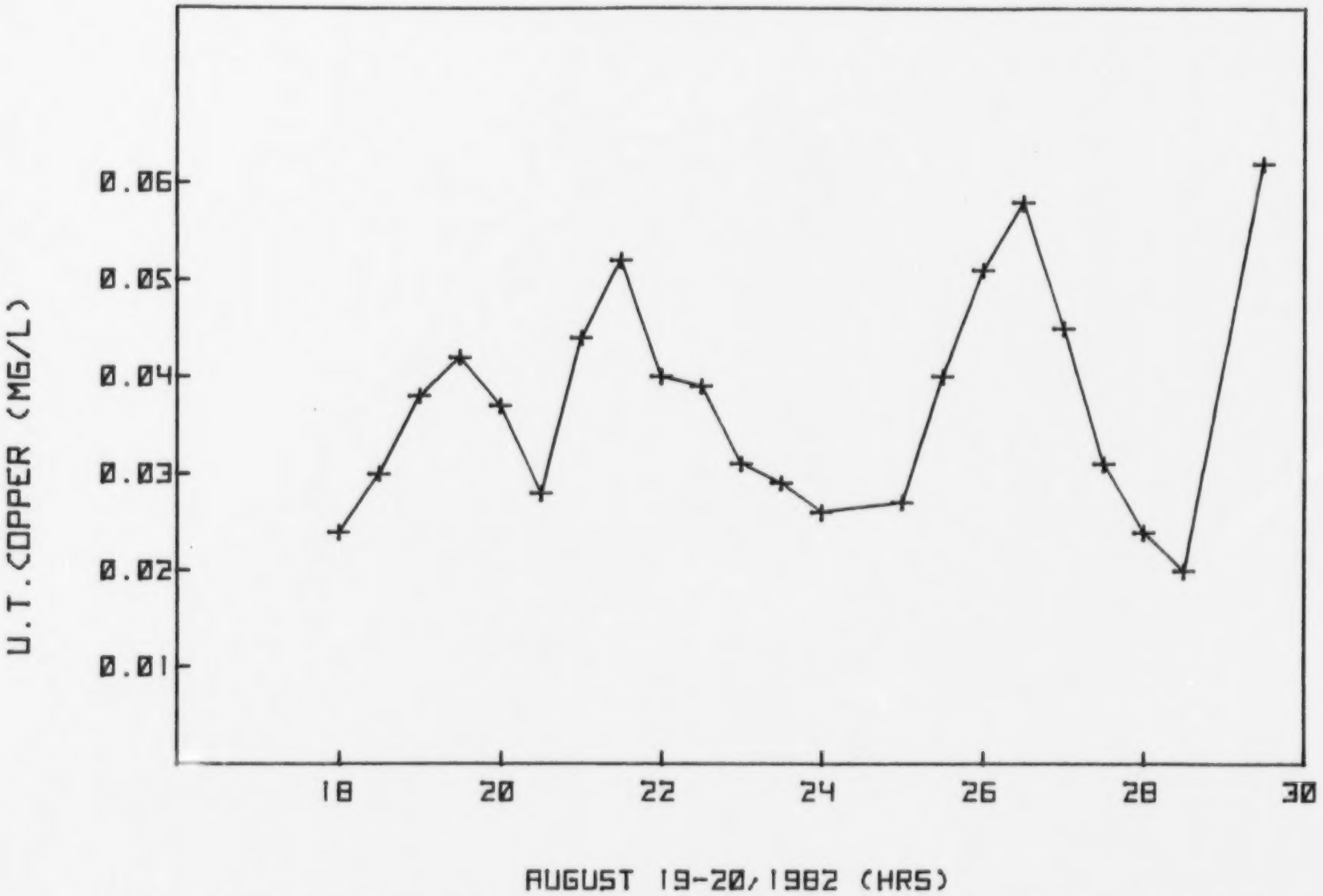

FIGURE 4b : VARIATION OF COPPER CONCENTRATION WITH TIME AT HAMILTON STP DURING RUNOFF SAMPLING PERIOD

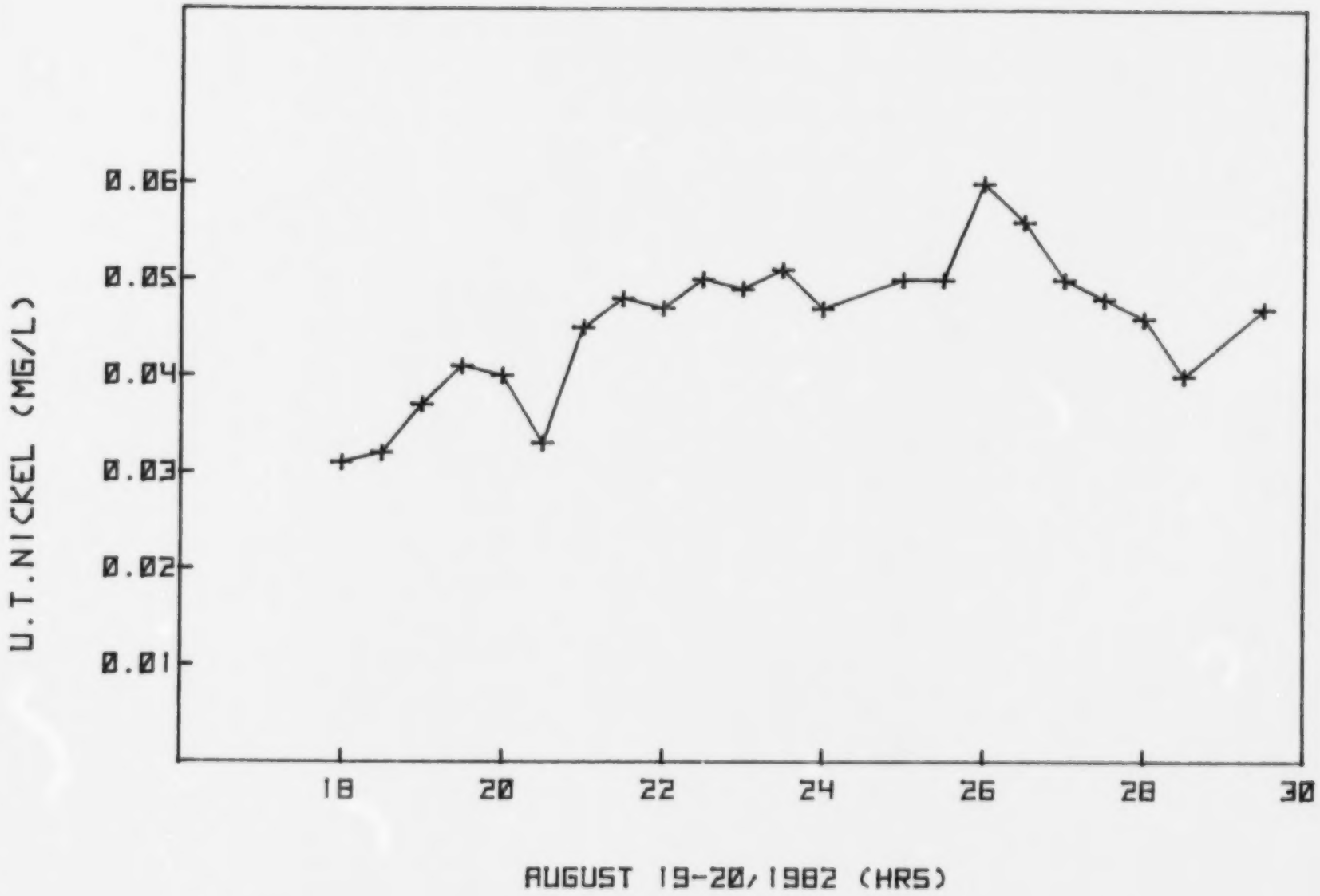

FIGURE 4c : VARIATION OF NICKEL CONCENTRATION WITH TIME AT HAMILTON STP DURING RUNOFF SAMPLING PERIOD

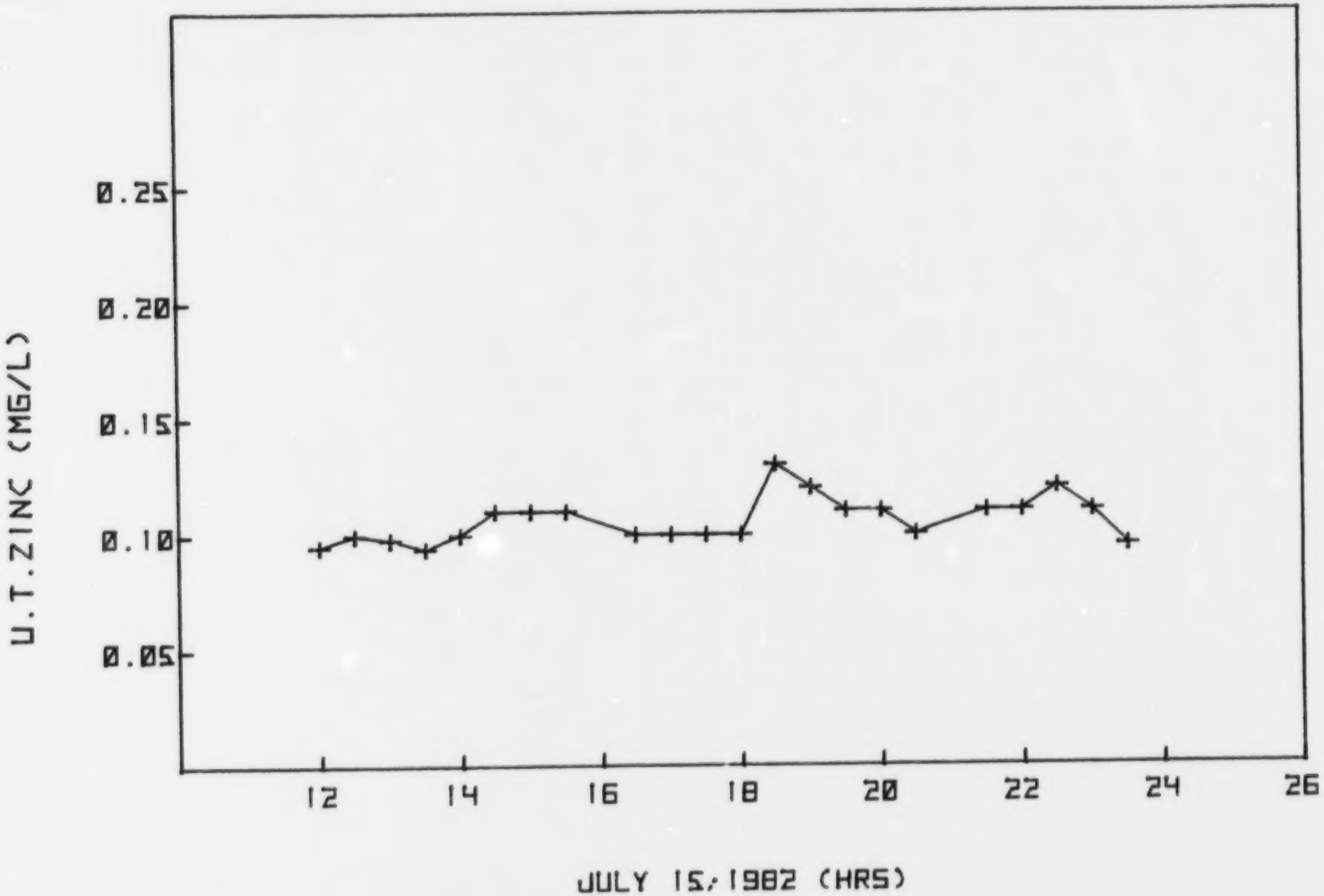

FIGURE 5a : VARIATION OF ZINC CONCENTRATION WITH TIME AT BURLINGTON STP DURING DRY WEATHER COLLECTION PERIOD

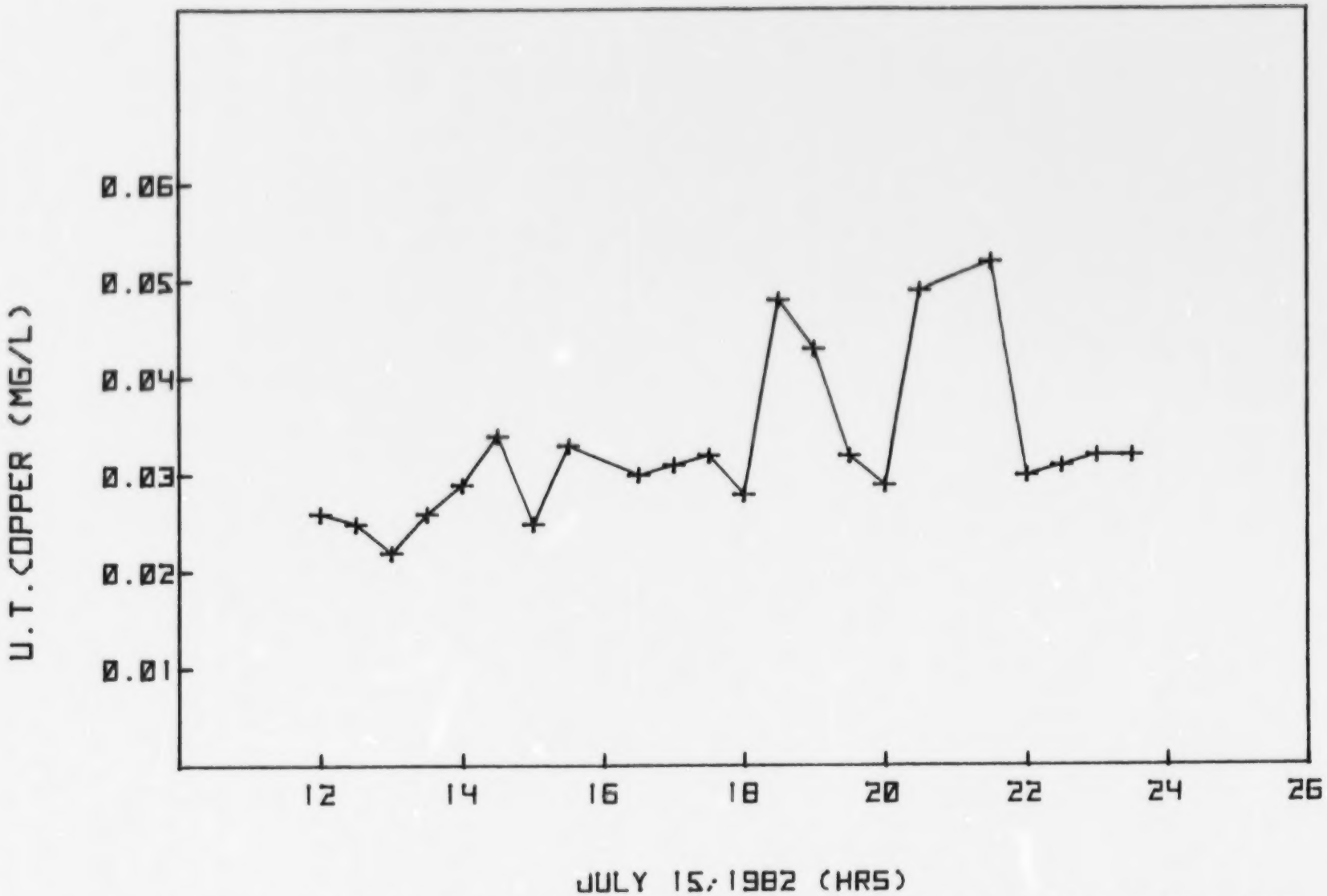

FIGURE 5b : VARIATION OF COPPER CONCENTRATION WITH TIME AT BURLINGTON STP DURING DRY WEATHER COLLECTION PERIOD

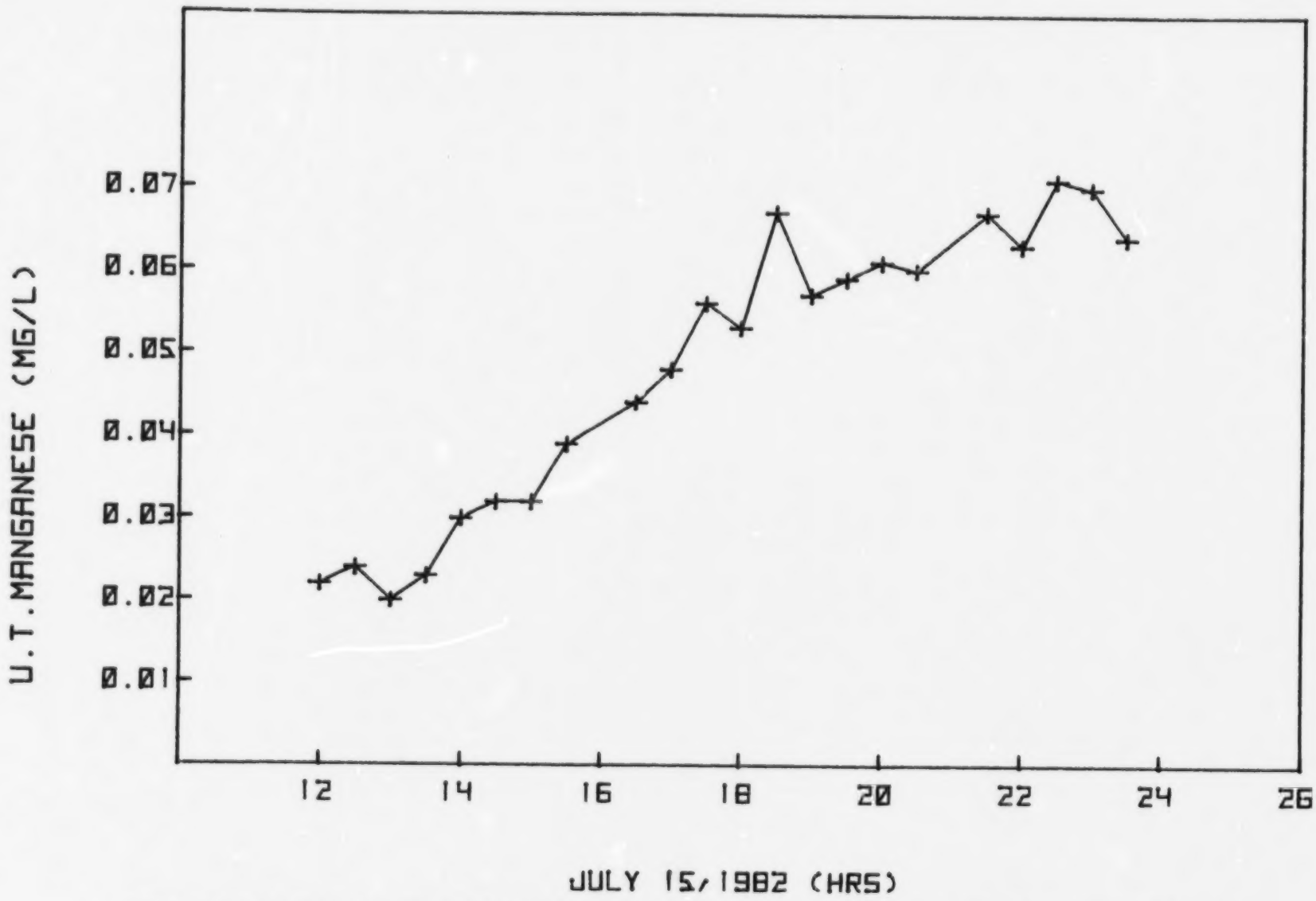

FIGURE 5c : VARIATION OF MANGANESE CONCENTRATION WITH TIME AT BURLINGTON STP DURING DRY WEATHER COLLECTION PERIOD

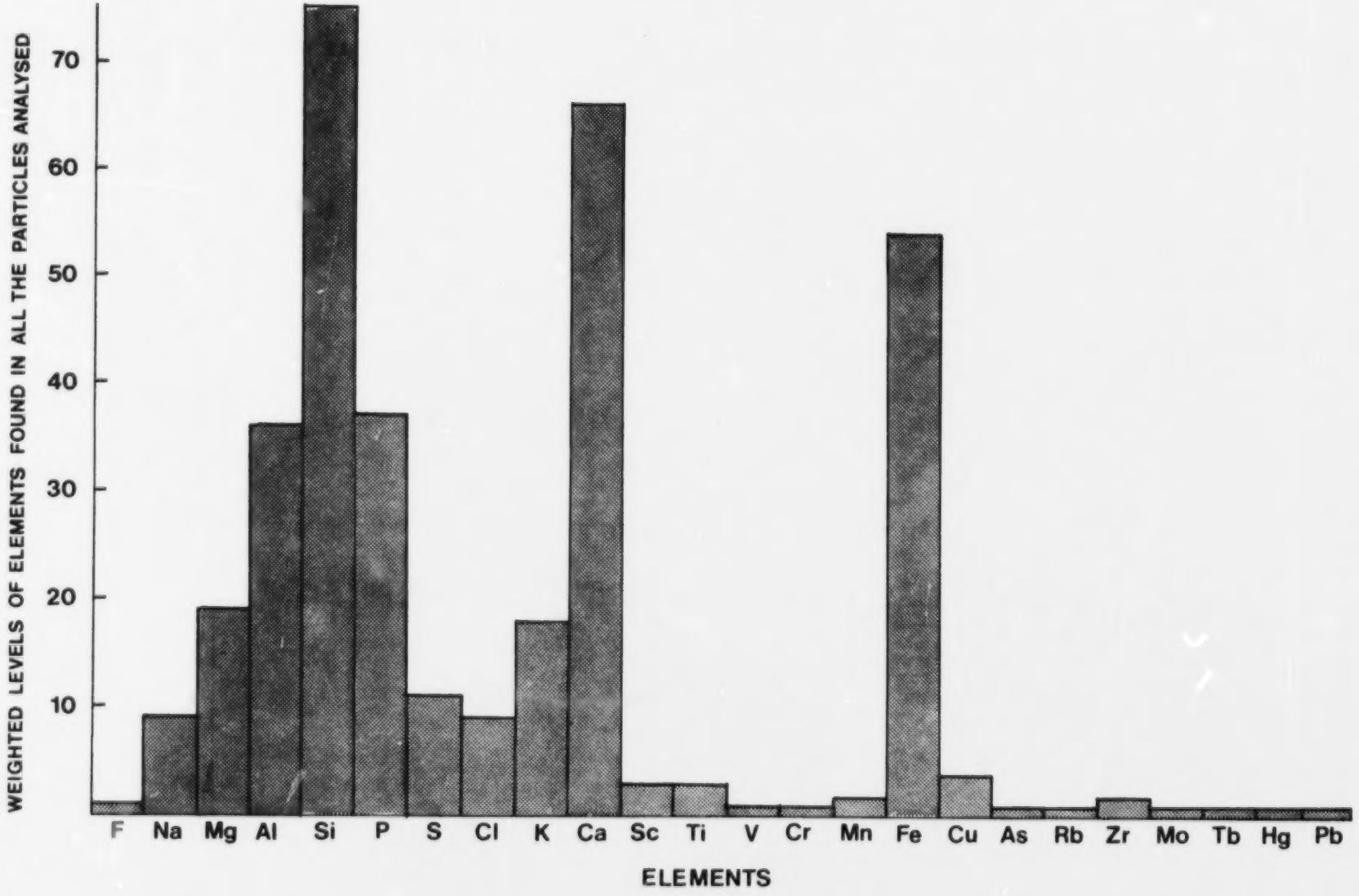
WEIGHTED LEVELS OF ELEMENTS FOUND IN ALL THE PARTICLES ANALYSED
70
60
50
40
30
20
10
F Na Mg Al Si P S Cl K Ca Sc Ti V Cr Mn Fe Cu As Rb Zr Mo Tb Hg Pb
ELEMENTS

FIGURE 6 : RESULTS OF ELECTRON MICROSCOPY ANALYSIS OF PARTICULATE SAMPLES FROM HAMILTON STP

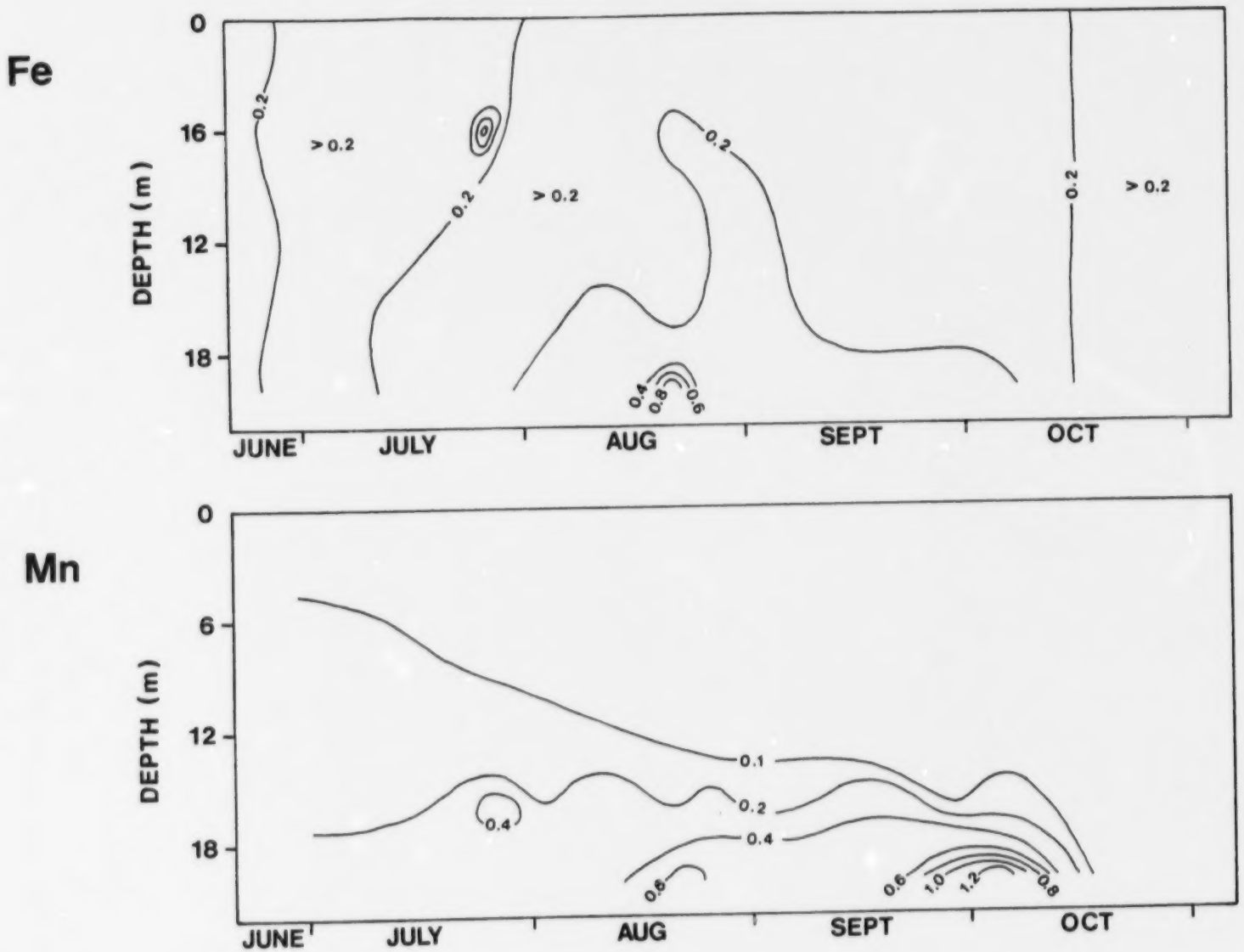

FIGURE 7 : ISOPLETHS OF IRON AND MANGANESE (mg/L) AT STATION 258, 1979